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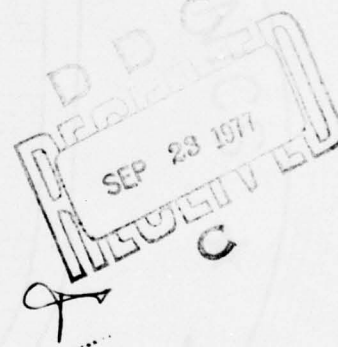
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THE ALPHA/BETA SILICON NITRIDE PHASE TRANSFORMATION

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CERAMICS RESEARCH DIVISION

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ABSTRACT

The literature on the relevance of the α/β silicon nitride transformation to hot pressing of silicon nitride ceramics is briefly reviewed as are crystal structure data for the two phases. Also mentioned are published results on the kinetics of the α/β phase transformation.

The kinetics of the transformation were determined by quantitative X-ray analysis on low and high purity silicon nitride powders at 1600 C. The addition of magnesia enhanced the transformation rate while the addition of yttria did not. It is concluded that the transformation proceeds via a solution-precipitation mechanism and that α and β silicon nitride are respectively low and high temperature forms.

CONTENTS

INTRODUCTION

Objectives of this Work

Early work on silicon nitride showed that the α crystallographic form can be converted to the β modification by heat treatment at temperatures exceeding 1500 C.[1,2] Thompson and Pratt[3] confirmed these findings and noted that prolonged heating of β silicon nitride in argon or nitrogen at temperatures from 1100 to 1350 C failed to bring about the reverse transformation.

Although the importance of the transformation to the fabrication of high-strength, hot-pressed silicon nitride has been recognized,[4] its exact role has remained obscure. Coe et al.[4] reported that α silicon nitride powder could be densified without transformation; they added, however, that high strength was only achieved through the phase transformation. Lumby and Coe[5] further emphasized the importance of the transformation to hot pressing. It was suggested by others that strength enhancement was a result of transformation-induced grain refinement,[6,7] but detailed mechanisms were not considered.

Certain microstructural features that may be transformation related have often been observed in hot-pressed silicon nitride. Among such features are elongated grains and preferred orientation.[8,9] Gazza,[10] reporting on the hot-pressing of silicon nitride with yttria additions, observed an abrupt change in microstructure that appeared to be associated with the transformation.

The importance of the α/β phase transformation to silicon nitride technology is clear. The purposes of this report are to review the literature on the α/β transformation, to present additional experimental results, and to evaluate this information in view of existing knowledge on the general subject of phase transformations.

Review of Crystal Structures

Although it is not intended to discuss the crystal structures of α and β silicon nitride in detail, disagreement in the literature on this subject makes it necessary to briefly review structural aspects that may relate to the transformation mechanism.

1. TURKDOGAN, E. T., BILLS, P. M., and TIPPETT, V. A. *Silicon Nitrides: Some Physicochemical Properties.* J. Appl. Chem., v. 8, 1958, p. 296-302.
2. FORGENG, W. D., and DECKER, B. F. *Nitrides of Silicon.* Trans. AIME, v. 212, 1958, p. 343-348.
3. THOMPSON, D. S., and PRATT, P. L. *The Structure of Silicon Nitride.* Science of Ceramics, v. 3, edited by G. H. Stewart. New York: Academic Press, 1967, p. 33-51.
4. COE, R. F., LUMBY, R. J., and PAWSON, M. F. *Some Properties and Applications of Hot-Pressed Silicon Nitride.* Special Ceramics, v. 5, edited by P. Popper, Manchester, England: BCRA, 1972, p. 361-375.
5. LUMBY, R. J., and COE, R. F. *The Influence of Some Process Variables on the Mechanical Properties of Hot-Pressed Silicon Nitride.* Proc. Brit. Ceram. Soc., no. 15, 1970, p. 91-101.
6. WILD, S., GRIEVESON, P., JACK, K. H., and LATIMER, M. J. *The Role of Magnesia in Hot-Pressed Silicon Nitride.* Special Ceramics, v. 5, edited by P. Popper, Manchester, England: BCRA, 1972, p. 377-382.
7. EVANS, A. G., and SHARP, J. V. *Microstructural Studies on Silicon Nitride.* J. Mater. Sci., v. 6, 1971, p. 1292-1302.
8. TERWILLIGER, G. R., and LANGE, F. F. *Hot-Pressing Behavior of Si_3N_4.* J. Am. Ceram. Soc., v. 57, 1974, p. 25-29.
9. NUTTALL, K., and THOMPSON, D. P. *Observations of the Microstructure of Hot-Pressed Silicon Nitride.* J. Mater. Sci., v. 9, 1974, p. 850-853.
10. GAZZA, G. E. *Silicon Nitride/Yttria: A Potential Gas Turbine Material.* Proc. Army Science Conf., West Point, NY, 22-25 June 1976.

After publication of preliminary structure data,[11,12] Ruddelesden and Popper[13] provided the first complete determinations of the α and β silicon nitride structures. Both forms were found to be hexagonal with formulas of $Si_{12}N_{16}$ for α and Si_6N_8 for β.

It was later proposed that α silicon nitride was necessarily an oxynitride of composition $Si_{11.5}N_{15}O_{0.5}$,[14] and a subsequent structure determination[15] was consistent with this theory. Additional supporting evidence was provided by a thermodynamic study[16] and by work reported by Feld et al.[17]

Recent results, however, do not support the oxynitride theory. Priest et al.[18] reported an oxygen content of only 0.30 w/o for α silicon nitride prepared by chemical vapor deposition (CVD),* an amount substantially less than the 0.90 to 1.48 w/o that is required for the oxynitride. It was also reported that this material was untransformed to β after heating for several hours at 1800 C in nitrogen at a pressure of 2 MPa. Edwards et al.[19] found oxygen contents in reaction-bonded silicon nitride that were at most half as large as required for the oxynitride formula to be correct. More recently, Kijima et al.[20] measured oxygen contents of 0.05 and 0.09 w/o on α silicon nitride single crystals.

Redeterminations of the α crystal structure by Kohatsu and McCauley[21] and by Kato et al.[22] agree with the determination of Marchand et al.[23] but not with the work of Wild et al.[15] In none of the former determinations was it necessary to assume that α comprised anything but Si_3N_4. In addition, the determination of Kato et al.[22] was done on the same crystal known, from analytical work,[20] to have a low oxygen content (0.05 w/o).

The crystal structures of the α and β forms of silicon nitride are illustrated in Figure 1. For convenience, both structures can be visualized as being formed from basic units comprising puckered rings, each ring containing four

*United Technologies Corporation, East Hartford, Ct., USA.

11. POPPER, P., and RUDDLESDEN, S. N. *Structures of the Nitrides of Silicon and Germanium.* Nature, v. 179, 1957, p. 1129.
12. HARDIE, D., and JACK, K. H. *Crystal Structure of Silicon Nitride.* Nature, v. 180, 1957, p. 332-333.
13. RUDDLESDEN, S. N., and POPPER, P. *On the Crystal Structures of the Nitrides of Silicon and Germanium.* Acta Cryst., v. 11, 1958, p. 465-468.
14. GRIEVESON, P., JACK, K. H., and WILD, S. *The Crystal Structures of Alpha and Beta Silicon and Germanium Nitrides.* Special Ceramics, v. 4, edited by P. Popper, Manchester, England: BCRA, 1968, p. 237-238.
15. WILD, S., GRIEVESON, P., and JACK, K. H. *The Crystal Structures of Alpha and Beta Silicon and Germanium Nitrides.* Special Ceramics, v. 5, edited by P. Popper, Manchester, England: BCRA, 1972, p. 385-396.
16. COLQUOHOUN, I., WILD, S., GRIEVESON, P., and JACK, K. H. *Thermodynamics of the Silicon-Oxygen-Nitrogen System.* Proc. Brit. Ceram. Soc., no. 22, 1973, p. 207-227.
17. FELD, H., ETTMAYER, P., and PETZENHAUSER, I. *Sauerstoffstabilisierung von α-Si_3N_4.* Ber. Deut. Keram. Ges., v. 51, 1974, p. 127-131.
18. PRIEST, H. F., BURNS, F. C., PRIEST, G. L., and SKAAR, E. C. *Oxygen Content of Alpha Silicon Nitride.* J. Amer. Ceram. Soc., v. 56, 1973, p. 395.
19. EDWARDS, A. J., ELIAS, D. P., LINDLEY, M. W., ATKINSON, A., and MOULSON, A. J. *Oxygen Content of Reaction-Bonded α-Silicon Nitride.* J. Mater. Sci., v. 9, 1974, p. 516-517.
20. KIJIMA, K., KATO, K., INOUE, Z., and TANAKA, H. *Oxygen Content of α-Si_3N_4 Single Crystals.* J. Mater. Sci., v. 10, 1975, p. 362-363.
21. KOHATSU, I., and McCAULEY, J. W. *Reexamination of the Crystal Structure of α-Si_3N_4.* Mater. Res. Bull., v. 9, 1974, p. 917-920.
22. KATO, K., INOUE, Z., KIJIMA, K., KAWADA, I., TANAKA, H., and YAMANE, T. *Structural Approach to the Problem of Oxygen Content in Alpha Silicon Nitride.* J. Amer. Ceram. Soc., v. 58, 1975, p. 90-91.
23. MARCHAND, R., LAURENT, Y., and LANG, J. *Structure of α-Silicon Nitride.* Acta Cryst., v. B25, 1969, p. 2157-2160.
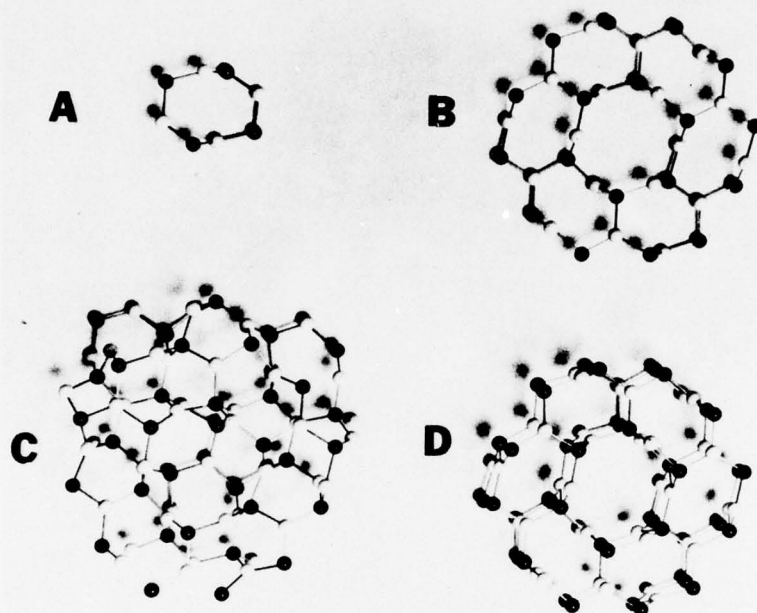
Figure 1. Models illustrating the crystal structure of silicon nitride. The dark balls represent silicon and the light ones nitrogen. (A) Eight-membered puckered ring. (B) Six puckered rings joined to form a basal plane sheet common to both structures. (C) Alpha silicon nitride. (D) Beta silicon nitride.

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silicon and four nitrogen atoms. Six of these rings join to form a sheet containing a large central hole. These basal plane sheets are sufficient to construct the entire crystal structures of both α and β silicon nitride.

As shown in Figure 1 the β structure comprises the sheets stacked atop each other in the sequence A, A, A, etc. The β structure is relatively unstrained and contains large channels as seen in the figure. In the α structure, the sheets are stacked alternately right side up and upside down in the sequence A, B, A, B, etc. The α structure is somewhat strained and distorted as compared to the β structure. The large channels evident in the β structure are absent in the α structure. Despite the differences, the first coordination is the same in each structure.

Literature on Transformation

The published literature includes no results of systematic, quantitative studies of the kinetics of the α/β transformation. The data included here are therefore generally from work in which the study of the transformation was of secondary interest.

Coe et al.[4] reported a linear relationship between percentage of β and log time for silicon nitride powder hot pressed with 1% magnesia at 1740 C. Naruse et al.[24] presented data on transformation versus temperature for three-hour heat treatments of pressed pellets at temperatures from 1300 to 1800 C. Some isothermal data were given at 1600 C but the results appear erratic. A few additional data were published by Weston and Carruthers[25] for hot-pressed material and by Inomata[26] for pressed pellets. The results of Feld et al.[17] were obtained on specimens that were apparently contaminated with silicon carbide and silicon oxynitride. In none of these studies was the transformation mechanism considered.

Wild et al.[6] proposed that, since they considered α to be an oxynitride, the transformation involved a chemical reaction between α and enstatite (formed by reaction of the magnesia additive with silica) as follows:

$$4Si_{11.5}N_{15}O_{0.5}(\alpha) + Mg_2SiO_4 = 15Si_3N_4(\beta) + 2MgSiO_3.$$
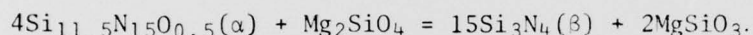
A detailed interpretation of the mechanism, however, was not given.

In view of the probable effect of the solubility of silicon nitride in oxide melts on the transformation, it is pertinent to review evidence for such solubility. Jack[27] has demonstrated solubility of silicon nitride in molten magnesium silicates. Nuttall and Thompson, in a TEM (transmission electron microscopy) study of hot-pressed silicon nitride, observed a hexagonal grain that appeared to have grown from a melt. Kossowsky,[28] in a wetting study, also reported that silicon nitride was soluble in molten magnesium silicate. Also consistent with this evidence are proposals that sintering in the silicon nitride-magnesia system occurs via a liquid phase mechanism.[28-30]

The TEM observations of Drew and Lewis[31] strongly support their conclusion that the transformation occurs via a solid/liquid/solid mechanism. The same authors[32] also presented convincing microstructural evidence for the formation of β' silicon aluminum oxynitride compounds by a similar mechanism.

24. NARUSE, W., NOJIRI, M., and TADA, M. *Formation Conditions and Properties of the Two Crystal Phases of Silicon Nitride.* Nippon Kinzoku Gakkaishi, v. 35, 1971, p. 731-738.
25. WESTON, R. J., and CARRUTHERS, T. G. *Kinetics of Hot Pressing of Alpha Silicon Nitride Powder with Additives.* Proc. Brit. Ceram. Soc., no. 22, 1973, p. 197-206.
26. INOMATA, Y. *Stability Relationships in the System of β-Si$_3$N$_4$-α-Si$_3$N$_4$-Si$_2$N$_2$O and their Structural Changes by Heating Above 1600 C.* Yogyo Kyokai Shi, v. 82, 1974, p. 522-526.
27. JACK, K. H. *The Production of High-Temperature, High-Strength Nitrogen Ceramics.* Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Chestnut Hill, MA: Brook Hill Publishing Co., 1974, p. 265-286.
28. KOSSOWSKY, R. *Wetting of Silicon Nitride by Alkaline-Doped MgSiO$_3$.* J. Mater. Sci., v. 9, 1974, p. 2025-2033.
29. TERWILLIGER, G. R., and LANGE, F. F. *Pressureless Sintering of Si$_3$N$_4$.* J. Mater. Sci., v. 10, 1975, p. 1169-1174.
30. BOWEN, L. J., WESTON, R. J., CARRUTHERS, T. G., and BROOK, R. J. *Mechanisms of Densification During the Pressure Sintering of α-Silicon Nitride.* Ceramurgia International, v. 2, 1976, p. 173-176.
31. DREW, P., and LEWIS, M. H. *The Microstructures of Silicon Nitride Ceramics During Hot-Pressing Transformations.* J. Mater. Sci., v. 9, 1974, p. 261-269.
32. DREW, P., and LEWIS, M. H. *The Microstructures of Silicon Nitride/Alumina Ceramics.* J. Mater. Sci., v. 9, 1974, p. 1833-1838.

EXPERIMENTAL PROCEDURES

Materials

The majority of the experiments were done with powder* containing 85 w/o of the α phase. This powder was nominally 99% pure and its surface area was 1.57 m^2/g. A few experiments were done on 100% α silicon nitride powder obtained by pulverizing thin slabs of material prepared by CVD. Because of the scarcity of this material, powder characterization was impossible.

For certain experiments, magnesia[†] and yttria[‡] were added to the silicon nitride powders. The powders were mixed by shaking in plastic containers. One experiment was conducted with an addition of silica powder from an unknown source.

Heating Procedures

A few preliminary experiments were done in an induction furnace comprising a graphite susceptor and graphite and zirconia refractories contained in a fused silica tube. However, a system consisting of a high-purity alumina muffle tube inside an inductively heated graphite susceptor was used for the rest of the experiments. All of the experiments were conducted in an atmosphere of flowing nitrogen. In the alumina system, the gas was dried by passing it through a phosphorous pentoxide drying tube.

The containers that were used were graphite crucibles with graphite lids. For the first series of runs, the inside of the crucible was coated with boron nitride to minimize reactions between the container and the powder. This precaution seemed unnecessary, however, and further runs were done without additional coatings.

The crucible and its contents were weighed before and after each run. At the beginning of a run, the crucible was loaded into the furnace and the system evacuated and backfilled twice. The furnace was then heated to about 1400 C in about 2 hours and held until the temperature stabilized. The temperature was then quickly raised to 1600 C and the system held at that temperature for the desired time. At periodic intervals, a portion of the specimen was removed for examination with the remainder being used for further heat treatment. All temperature measurements were done with a calibrated optical pyrometer.**

X-Ray Analysis

The proportions of α and β silicon nitride in the specimens were determined by quantitative X-ray analysis using CuK_α radiation.[33] Analyses were done on powder specimens packed into aluminum holders.

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33. GAZZARA, C. P., and MESSIER, D. R. *Quantitative Determination of Phase Content of Silicon Nitride by X-Ray Diffraction Analysis.* Army Materials and Mechanics Research Center, AMMRC TR 75-4, February 1975.

Microscopy

Photomicrographs of the various powder specimens were obtained with a scanning electron microscope.* Specimens were prepared by sprinkling powder on holders that had been coated with shellac diluted 100:1 with ethanol. It was found best to let the shellac mixture dry 1 to 2 minutes before applying the powder. The specimens were then coated with Pd-Au alloy or pure Pd for examination in the microscope.

RESULTS

X-Ray Technique

Table 1 shows the results of several determinations by X-ray diffraction analysis[33] of the phase content of the commercial silicon nitride powder. The specimens that were run on glass slides were prepared by dispersing a small amount of powder in a Formvar-chloroform solution. The mixture was then applied to the slide and allowed to dry, leaving a thin layer on the slide. It should be noted that the use of this preparation technique gave rather high standard deviations, particularly for the β phase, and lower α values than were obtained using the packed powder specimens. On the other hand, the packed powder results on two instruments, with different receiver slits, were in good agreement. The absence of silicon peaks in three of the runs is probably a result of the use of low counting rates for those runs.

Transformation Data

Table 2a presents the data that were obtained on the transformation kinetics in preliminary experiments in systems known to be leaking and contaminated with various deposits from previous runs with other materials. While estimates of the quality of the atmospheres in these systems are subjective, it is believed that the system used for Run 1 contained more oxygen than did the one used for Run 2. The largest amount of silicon carbide observed in any of the runs was produced in Run 1. Whenever silicon carbide was found, it was invariably in the 2H form.

Table 1. EFFECTS OF SPECIMEN PREPARATION AND INSTRUMENT VARIABLES ON THE DETERMINATION BY X-RAY ANALYSIS OF α/β RATIO IN AME SILICON NITRIDE POWDER

Run	X-Ray Instrument	Receiver Slit Deg.	Specimen Preparation	α-Si$_3$N$_4$ w/o	α % Std Deviation	β-Si$_3$N$_4$ w/o	β % Std Deviation	Si w/o
A	G.E.	0.2	Packed Powder	85.1	7.7	14.5	4.2	0.4
B	Philips	0.2	Packed Powder	85.8	6.8	14.2	7.8	-
C	Philips	0.1	Packed Powder	85.2	9.6	14.8	11.7	-
D	Philips	0.2	Powder on Glass Slide	84.1	5.2	15.4	15.1	0.5
E	Philips	0.2	Powder on Glass Slide (New Specimen)	82.2	9.0	17.8	25.0	-

*Stereoscan S-600, Cambridge Instruments Ltd, Cambridge, U.K.

Table 2. PHASE TRANSFORMATION DATA AT 1600 C ON SILICON NITRIDE POWDER

Run	Total Time (hours)	β-Si$_3$N$_4$ w/o	Other Phases*	Remarks
a.	**In contaminated systems**			
1	0.0	14.6	-	Fused SiO$_2$ tube, system
	1.0	25.6	2H SiC (m)	leaking badly and contaminated
	2.0	32.4	2H SiC (m-s)	
	4.0	40.2	2H SiC (s)	
2	0.0	15.9	-	Al$_2$O$_3$ tube, system leaking
	1.0	27.7	-	and contaminated
	2.0	29.6	-	
	4.0	32.9	-	
b.	**As-received and with oxide additives**			
3	0.0	14.6	-	
	0.5	20.3	-	
	1.5	23.4	-	
	3.0	25.3	2H SiC† (vw)	No additive
	6.0	30.5	2H SiC† (vw)	
	9.0	34.2	2H SiC (w)	
	10.0	36.2	2H SiC (w)	
4	0.5	29.8	-	
	1.0	34.1	-	
	2.0	38.0	-	*1 w/o MgO added*
	4.0	45.2	-	
	4.75	46.3	-	Furnace rebuilt after 4 hr
	8.0	47.9	2H SiC† (vw)	
	10.0	48.5	2H SiC† (vw)	Sintering occurred
5	0.75	38.6	-	
	1.5	43.4	-	
	3.0	46.7	-	1 w/o MgO added
	5.0	51.5	2H SiC† (vw)	
	7.0	54.2	2H SiC† (vw)	Sintering occurred
	9.0	57.6	2H SiC (vw)	
6	1.0	17.2	Si$_2$N$_2$O (w)	5 w/o SiO$_2$ added
7	0.5	46.8	Unidentified (w)	
	1.0	64.1	"	10 w/o MgO added
	2.0	86.5	"	
	4.0	100	"	Sintering occurred
8	0.5	19.6	Y$_2$O$_3$, J‡	
	1.0	22.0	"	
	2.0	22.2	"	
	4.0	25.7	"	10 w/o Y$_2$O$_3$ added
	6.0	26.7	"	
c.	**Prepared by CVD process**			
9	2.0	0.0	2H SiC (w-m)	No additive
	6.0	0.0	2H SiC (s)	
10	0.5	3.5	-	
	1.0	3.7	-	
	2.0	3.8	2H SiC†	10 w/o MgO added
	4.0	4.3	-	Sintering occurred
	8.0	4.5	2H SiC (m)	

*(m) = medium
(m-s) = medium-strong
(s) = strong
(vw) = very weak
(w) = weak
†Probably present
‡Plus unidentified peaks

Table 2b lists the majority of the experimental results. All these experiments were done with gas-tight alumina tubes that had not been previously used for other purposes. As noted in the table, several extraneous phases were observed in some of the products. Among them was silicon oxynitride in the case when silica was added, and "J" phase when yttria was the additive. The J phase was indexed from the data of Rae et al.[34] The unidentified lines in Run 7 (10 w/o magnesia added) may have been from crystalline magnesium silicate phases; no attempt was made to index them. Table 2c gives the results of experiments done with the CVD powder. It should be noted that more silicon carbide was observed without the additive than with it as was generally the case. Furthermore, transformation occurred only when magnesia was added to the CVD powder.

Although some sintering occurred when magnesia was added (Table 2b and c), the transformation rate was unaffected by it. In one experiment, the transformation rate on a sintered piece was found to be the same as the rate on powder prepared by pulverizing a portion of that piece.

The transformation rate was also observed to be the same on portions of a specimen taken from the top and bottom parts of the crucible. As a check of the effect of possible vapor phase interactions on the transformation rate, a 2-mm-diameter hole was drilled in the crucible lid between the 9 and 10 hour times in Run 3. The hole had no apparent effect.

Some weight loss was observed in all of the runs, particularly in the "contaminated" systems; a weight loss of 5% occurred in 1 hour in Run 1. Some weight loss was attributable to the crucible and there was no apparent correlation between weight loss and transformation rate. The weight loss data are therefore not included in the tables.

Transformation Kinetics

Figure 2 compares transformation rates obtained in "contaminated" systems (Runs 1 and 2) with that obtained in a "clean" system (Run 3). All runs were conducted with the commercial powder as received. The rate curves are smooth and the rates are notably faster in the contaminated systems.

Figure 3 gives transformation curves for the commercial silicon nitride powder under various conditions. The curve for the undoped material is the same as the one given in Figure 2. It is evident that the transformation rate is highly dependent on the magnesia content of the specimen. The latter part of the curve for the 10 w/o magnesia specimen is dashed because the transformation was complete at some unknown point between 2 and 4 hours. Although the two curves for the 1 w/o magnesia specimens differ somewhat, both are clearly above the curve for the undoped material and below the one for the specimen containing 10 w/o magnesia. As seen in the figure, the addition of 10 w/o yttria had no apparent effect on the transformation rate at 1600 C, and the addition of 5 w/o silica had, if anything, a slight negative effect.

34. RAE, A. W. J. M., THOMPSON, D. P., PIPKIN, N. J., and JACK, K. H. *The Structure of Yttrium Silicon Oxynitride and Its Role in the Hot-Pressing of Silicon Nitride with Yttria Additions.* Special Ceramics, v. 6, edited by P. Popper, Manchester, England: BCRA, 1975, p. 347-360.
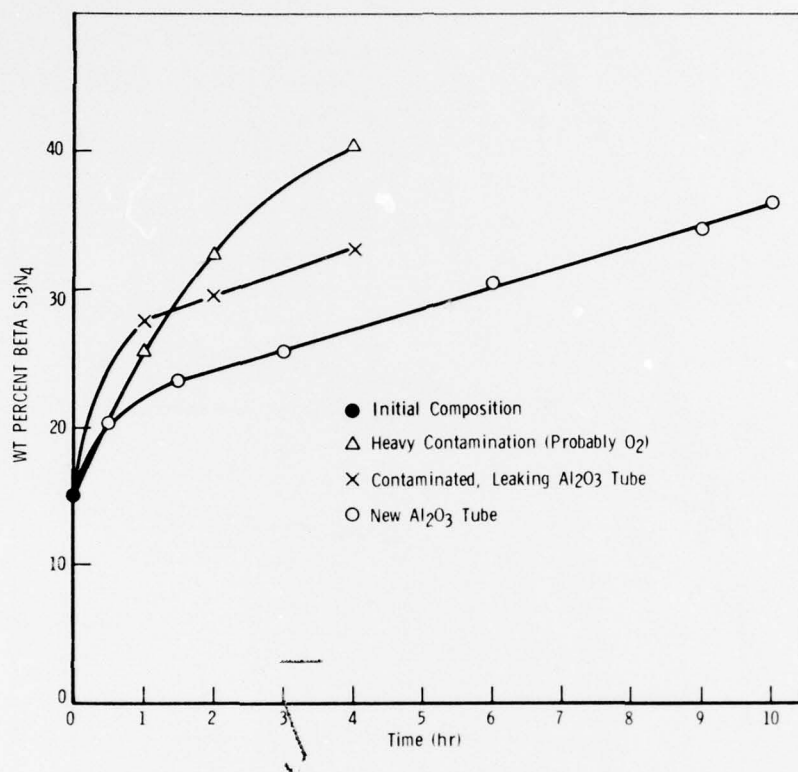
Figure 2. Differences in transformation rates of 85% alpha silicon nitride
powder heated in different systems in flowing nitrogen at 1600 C.

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Microscopy

Figure 4 shows the appearance of the commercial silicon nitride powder at
two magnifications. The powder is somewhat agglomerated and amorphous in appear-
ance and typically contains some high aspect ratio particles as evident in the
figure. For unknown reasons it was difficult to obtain good photomicrographs of
this powder.

Figure 5 shows powder specimens after heating in contaminated and clean
systems. Note the distinctive whiskers in the specimen heated in the contaminated
system. These whiskers were invariably associated with the presence of silicon
carbide in the specimen. The elongated grains in the powder heated in the clean
system resemble the ones in the unheated powder (Figure 4). Since some silicon
carbide was detected in this specimen, however, it is possible that these grains
are also silicon carbide.

Figure 6 shows powder containing 1 w/o magnesia after partial transformation.
Note the typical size and shape of the grains in this and the following figures
as compared to those in the starting powder (Figure 4).

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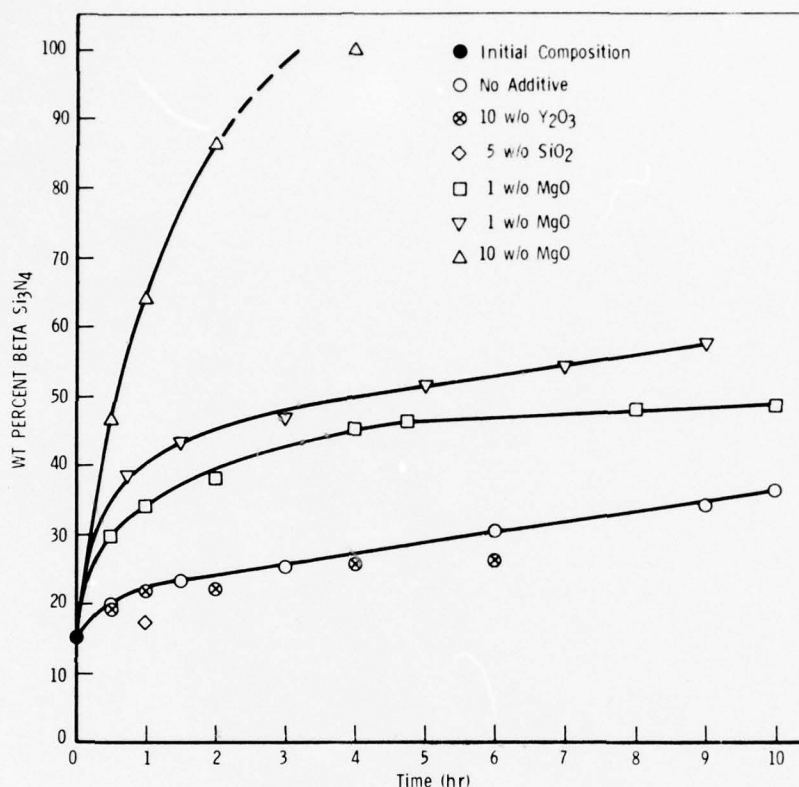
Figure 3. Effects of additives on the rate of transformation of 85% alpha
silicon nitride powder in flowing nitrogen at 1600 C.

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Figure 7 shows the appearance of the specimen containing 10 w/o magnesia
after partial and complete transformation. Many of the grains are log-shaped,
and some show hexagonal symmetry. The grain size shows no obvious correlation
with time of heating or magnesia content, and Figures 7c and 7d show a range of
grain sizes within the same specimen.

DISCUSSION OF RESULTS

X-Ray Technique

The X-ray technique that was used for quantitative analysis[33] was devised
to minimize the effects of preferred orientation. This is accomplished by
averaging seven α peaks, four β peaks, and two Si peaks. All the peaks are
normalized using weighting factors, and the standard deviations given in Table 1
are thus related to the degree of preferred orientation of each phase, i.e., in
the absence of preferred orientation, the standard deviation would be zero. It
is interesting to note that the standard deviations for the α phase do not differ
significantly in the five cases listed in Table 1 and that the β standard devia-
tions are high for the two specimens mounted on glass slides. The first three

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The literature on the relevance of the α/β silicon nitride transformation to hot pressing of silicon nitride ceramics is briefly reviewed as are crystal structure data for the two phases. Also mentioned are published results on the kinetics of the α/β phase transformation. The kinetics of the transformation were determined by quantitative X-ray analysis on low and high purity silicon nitride powders at 1600 C. The addition of magnesia enhanced the transformation rate while the addition of yttria did not. It is concluded that the transformation proceeds via a solution-precipitation mechanism and that α and β silicon nitride are respectively low and high temperature forms.

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(a) Mag. 1.3K   (b) Mag. 4.0K

5 μm   5 μm
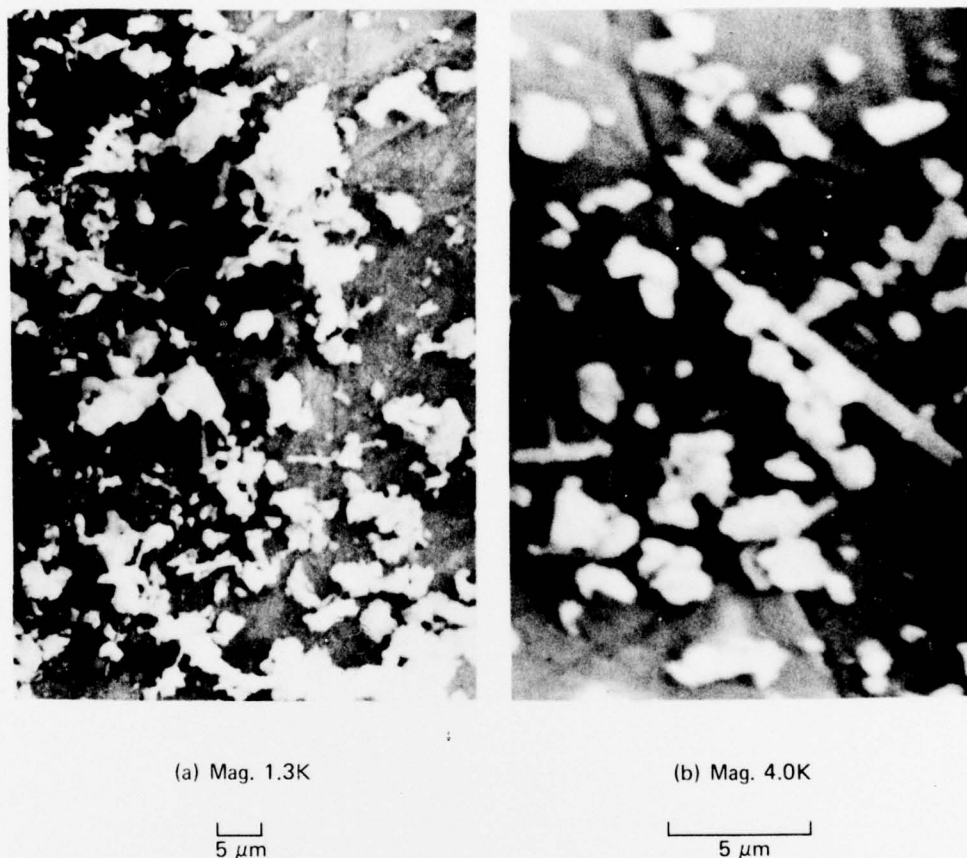
Figure 4. High alpha (85%) silicon nitride powder.

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phase content determinations are in good agreement, and despite the large amount of preferred orientation in the latter two, the values obtained are only 3% less in the worst case. It thus appears that the analysis procedure does indeed minimize preferred orientation effects, and that it can be used with considerable confidence.

Based upon the above results, all of the specimens that were analyzed were prepared by packing the powder into a holder rather than using glass slides. Standard deviations were determined for each run and, for the 85% α powder, the highest standard deviation for the β phase was only 13.1% with the majority being less than 10%. The CVD powder was coarsely ground and contained only small amounts of β phase; standard deviations in that case were as high as 35%. Nevertheless, Table 2c shows a small but consistent increase in β content with time for the specimen heated with magnesia.

The absence of silicon peaks in some of the determinations listed in Table 1 may be due to the use of low counting rates for those determinations. Because

11

(a)   (b)

⊢—⊣
5 μm
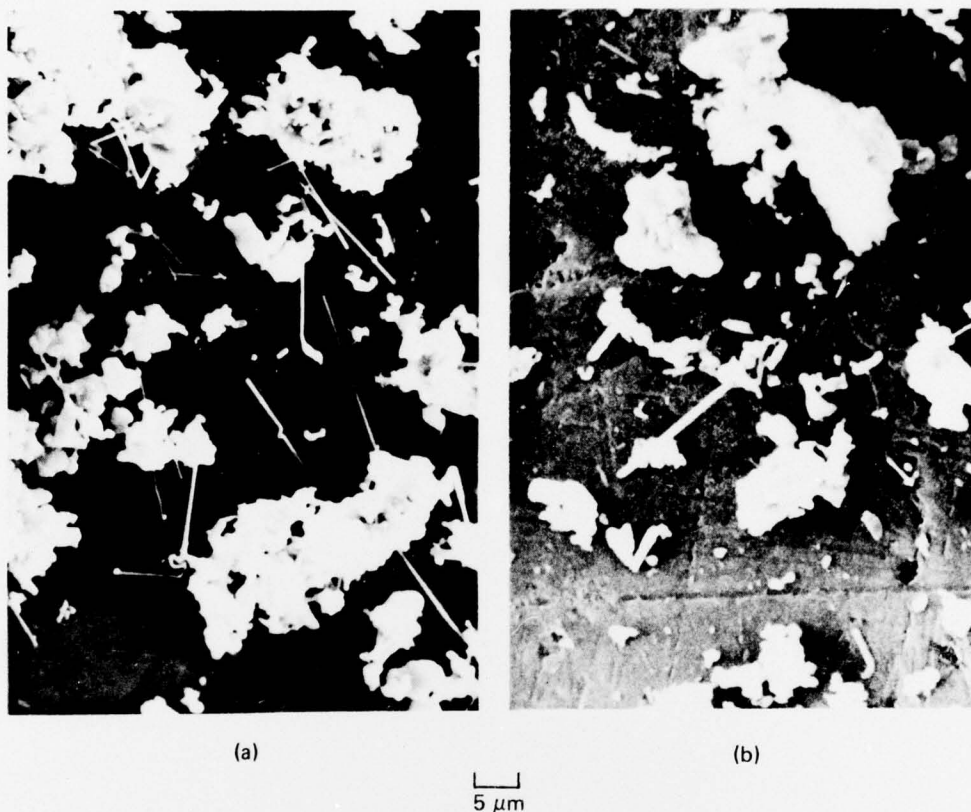
Figure 5. (a) Silicon carbide whiskers in silicon nitride powder heated for 4 hours at 1600 C
in a "contaminated" system. (b) Silicon nitride powder heated without
additives for 10 hours at 1600 C in a "clean" system.

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silicon was never observed in the heat-treated specimens, and the ratio of α to β
was of primary interest, this point appears irrelevant to interpretation of the
experimental results.

Although it is difficult to estimate quantitatively the precision of the
X-ray technique, the results suggest that it should be within 1% or so if reason-
able care is taken with specimen preparation and choice of instrument parameters.

Transformation Data

It is apparent from Table 2 that silicon carbide formation was often ob-
served, particularly in the system that was grossly contaminated (Table 2a). It
is also noteworthy that this phase was absent in specimens containing oxide
additives. Similar observations were reported by Colquohoun et al.[35] in a paper

35. COLQUOHOUN, I., THOMPSON, D. P., WILSON, W. I., GRIEVESON, P., and JACK, K. H. *The Determination of Surface Silica
and Its Effect on the Hot-Pressing Behaviour of Alpha-Silicon Nitride Powder.* Proc. Brit. Ceram. Soc., no. 22, 1973, p. 181-195.

5 μm
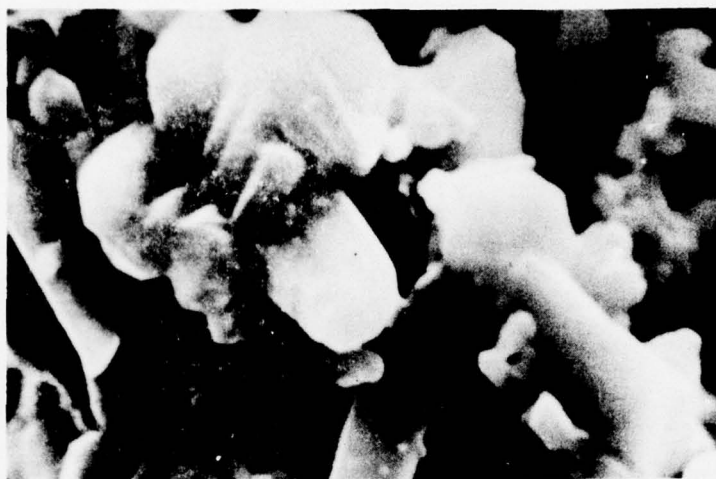
Figure 6. Silicon nitride powder containing 1 wt% MgO after heating
for 9 hours at 1600 C. The large grains are probably beta silicon nitride.
19-066-1509/AMC-76

concerned with the role of surface silica in the hot pressing of silicon nitride
powder. They explained that when the powder is heated, this silica volatilizes
as silicon monoxide which in turn reacts with the graphite container to produce
carbon monoxide. The latter then carburizes the silicon nitride as follows:

$$3CO(g) + Si_3N_4(s) = 2SiC(s) + N_2(g) + CO_2(g) + SiO(g)$$
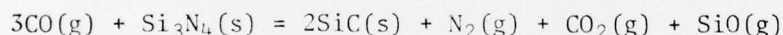
The above reaction produces more silicon monoxide which continues the cycle.
When, however, an oxide additive such as magnesia is used, it combines with the
silica to form magnesium silicates, thus reducing the activity of the silica and
suppressing the formation of silicon monoxide. In that case the formation of
silicon carbide is minimized.

The present results, however, indicate that the above explanation may be
oversimplified, for the addition of silica to the nitride (Run 6) did not produce
excess silicon carbide as would be expected from the above considerations. In
fact, silicon oxynitride was formed. It may therefore be possible that the mor-
phology and distribution of the silica also affect the chemical reactions that
occur.

The increased transformation rates in the contaminated systems (Figure 2)
may also be associated with the formation of silicon carbide. The analysis
technique that was used only determines the relative amounts of the silicon
nitride phases, and, if the α phase carburized preferentially, the effect would
be to increase the β/α silicon nitride ratio.

13
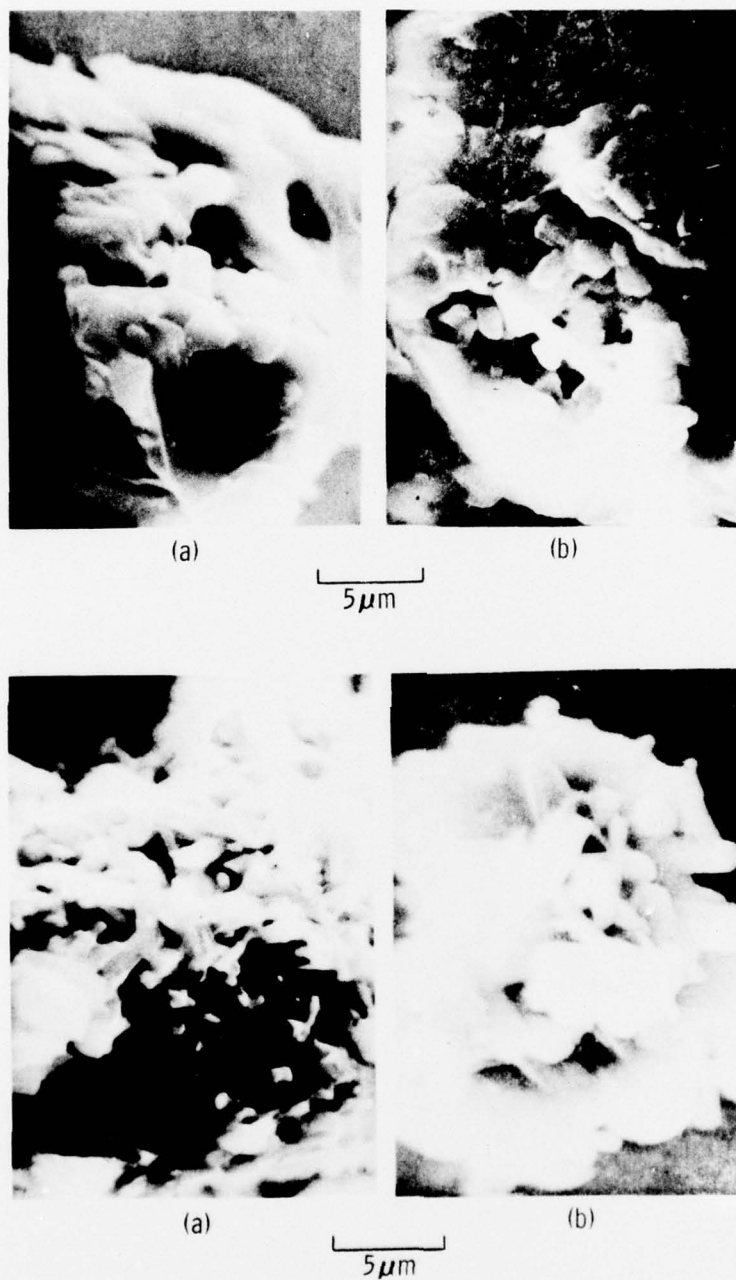
Figure 7. Silicon nitride powder containing 10 wt% MgO after conversion to the beta form by heating at 1600 C; (a) and (b) show partial conversion by heating for 0.5 hour; (c) and (d) show complete conversion by heating for 4 hours. Note the small grains in (c) and the hexagonal symmetry of some of the grains in (d).

7a+b. 19-066-1507/AMC-76   7c+d. 19-066-1505/AMC-76

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Transformation Kinetics

Because of the small amount of transformation, and considering the limits of precision of the X-ray analysis technique, the rate data for the CVD powder (Table 2c) are not given in a figure. It should be noted, however, that those data give no indication of an induction period which would be observed if nucleation were rate-controlling. That the transformation rate is much slower on the CVD powder than on the commercial powder may be because of the coarse particle size of the CVD powder. Although it was incompletely characterized, particles of the order of 30 to 40 μm diameter were observed in the CVD powder as compared to the 1-μm sized particles seen in the commercial powder (Figure 4). Other factors that may have contributed to the difference in transformation rate are impurities in the commercial powder and possible differences in silica content between the two powders.

The rather poor reproducibility of the repeat runs with 1 w/o magnesia added (Figure 3) is difficult to explain. The discrepancy is more than would be expected from errors in X-ray analysis and it may have resulted from rebuilding of the furnace between Runs 4 and 5. All temperature measurements were made with an optical pyrometer that was recalibrated frequently so it would be expected that furnace changes would have no effect. Considering the crudness of the mixing technique, it is also possible that the discrepency resulted from inhomogeneities in mixing of the additive with the silicon nitride powder. At any rate, the data are only being interpreted on a semiquantitative basis, and the observed differences with different magnesia additions are clearly beyond the limits of experimental error.

All the evidence in this study and in the literature strongly supports the conclusion of Drew and Lewis[31] that the α/β silicon nitride transformation occurs via a solution-precipitation mechanism. An early, tentative suggestion that a solid state mechanism is involved[7] can therefore be discounted. In view of present knowledge of crystal structure and available transformation data, a mechanism involving "deoxidation" of an oxynitride (α) to form the "pure" nitride (β)[6] is also unlikely.

As indicated in the Introduction, there is ample evidence in the literature for the solubility of silicon nitride in molten silicates as well as microstructural observations that are consistent with a solution-precipitation mechanism. The results presented in this report are also consistent with such a mechanism. The strong dependence of the transformation rate on the content of magnesia (Figure 3) suggests that the rate is proportional to the amount of magnesium silicate liquid that is present. It is also significant that the transformation rate at 1600 C was unaffected by the addition of yttria, another common hot-pressing aid.[10] These results can be easily rationalized by considering that the lowest eutectics occur at 1543 C in the magnesia-silica system[36] and at 1660 C

36. BOWEN, N. L., and ANDERSEN, O. *The Binary System MgO-SiO₂.* Amer. J. Sci., v. 37, 1914, p. 488-500.

in the yttria-silica system.[37] One would therefore not expect an enhanced trans-
formation rate in the Y.S. system until the temperature was above the eutectic
and liquid was formed.

That a certain amount of transformation occurred in the commercial powder
without additives must be attributed to the presence of impurities that react
with silica to form liquid phases. As already mentioned, Priest et al.[18] ob-
served no transformation whatsoever in high purity CVD silicon nitride heated to
a temperature as high as 1800 C. In this study, transformation occurred at
1600 C only when magnesia was added to the CVD powder. The observation of Jack[27]
that transformation occurs without magnesia additions is consistent with the
above observations if it is recognized that the powder used in his work contained
approximately the same impurity levels as the commercial powder used in this
study.

Microscopy

Whether or not the α/β transformation produces grain refinement[6,7] is still
unresolved. The observations reported here (Figures 4 to 7) show the development
of a relatively fine-grained (1 to 4 μm) material, but one with grains that are
somewhat larger than those in the starting powder. It is significant, however,
that extremely large grains were never observed; the high strength of the hot-
pressed material may therefore be a result of the development of a very uniform
fine-grained microstructure comprising β silicon nitride of high crystalline
perfection.

It seems unquestionable that the whiskers shown in Figure 5a are silicon
carbide. As discussed earlier, the use of additives suppresses the formation of
silicon carbide, and it should be noted that no such whiskers occur in the powders
heated with magnesia additions.

Although Lange[38] has suggested that the aspect ratios of the β grains in
hot-pressed silicon nitride are related to the β phase content of the starting
powder, the present results indicate that his explanation is oversimplified. For
example, in this investigation the formation of β silicon nitride was observed
even when phase pure α powder was used. In that case, the β phase could not
have grown on existing grains, and new nuclei must have formed.

Reaction Mechanism

The α/β transformation has been shown to follow first-order kinetics under
pressure sintering conditions[39] and Figure 8 shows the present data plotted in
such a manner. The assumed rate law is

37. TOROPOV, N. A., and BONDAR, I. A. *Silicates of the Rare Earth Elements. III. Phase Diagram for the Binary System Yttrium
Oxide-Silica.* Izv. Akad. Nauk. SSR. Otd. Khim. Nauk., no. 4, 1961, p. 544-550. *Silicates of the Rare Earth Elements. VI. Phase
Diagrams for the Binary Systems $Sm_2O_3 \cdot SiO_2$ and $Yb_2O_3 \cdot SiO_2$ and a Comparison of Them with the Silicates of Other Rare
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Sintering of α-Silicon Nitride.* Proc. NATO Inst. on Nitrogen Ceramics, Canterbury, England, 16-27 August 1976.

Figure 8. Log percent alpha versus time for phase transformation of 85%
alpha silicon nitride powder in flowing nitrogen at 1600 C.

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$$d\alpha/dt = k\alpha,$$

where α is the weight percent of α silicon nitride remaining in the specimen.
It is apparent that the data fit such a plot reasonably well, but because of the
usual complications involved in solid state reactions, detailed speculation re-
garding the exact transformation mechanism is unwarranted from the present
results.

GENERAL DISCUSSION

It has been suggested from structural considerations that the α/β trans-
formation should be reconstructive,[3,40] and all available evidence indicates
that it can be classified as a reconstructive transformation of second coordina-
tion.[41] Such transformations involve breaking bonds, but the first coordination
is the same in each structure. Because of the structural rearrangement that is
required, the kinetics of the process are sluggish, and a solvent is often needed
to enable the transformation to occur.[42] Other examples of this type of trans-
formation are the ones between any pair of the set quartz-tridymite-cristobalite
and the würtzite-sphalerite transformation.[42]

40. HENDERSON, C. M. B., and TAYLOR, D. *Thermal Expansion of the Nitrides and Oxynitride of Silicon in Relation to Their Structures.* Trans. and J. Brit. Ceram. Soc., v. 74, 1975, p. 49-53.

41. BUERGER, M. J. *Crystallographic Aspects of Phase Transformations* in Phase Transformations in Solids, edited by R. Smoluchowski, J. E. Mayer, and W. A. Weyl, New York: John Wiley and Sons, 1951, p. 183-211.

42. VERMA, A. R., and KRISHNA, P. *Polymorphism and Polytypism in Crystals.* New York: John Wiley and Sons, 1966.

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The present results support the assumption that β silicon nitride is the stable form at 1600 C. Ample evidence exists for the solubility of both forms of silicon nitride in molten silicates,[8,9,27-30] and it would be expected that a solution saturated with the unstable form (α) would be supersaturated with respect to the stable form (β) at a temperature above the transition point.[42] The proposed solution-precipitation transformation mechanism is thus entirely consistent with qualitative thermodynamic arguments regarding the stabilities of the two phases.

It seems pertinent to further consider the silicon nitride transformation in terms of what is known about other systems,[42] specifically in regard to whether or not α silicon nitride is metastable at all temperatures,[40] and as to whether or not α is the low-temperature and β the high-temperature form. In general, the high-temperature form tends to be more symmetrical than the low-temperature form and Figure 1 indicates that such is the case for β silicon nitride. From entropy considerations, one expects the high-temperature form to have greater open spaces available for thermal motion and to have lower density. The β silicon nitride appears to satisfy the former criterion, but not the latter; the density of α ($3185 \ kg/m^3$) is slightly less than that of β ($3196 \ kg/m^3$).

From phase transformation theory, one can extract free energy arguments that are also consistent with α silicon nitride being the low-temperature form for, at absolute zero, the form having the least internal energy E would be the more stable.[42] This internal energy at $T = 0$ is given by

$$E = -U + 1/2 \ h\nu$$

where U is the structure energy and $1/2 \ h\nu$ is the zero-point energy. At absolute zero, the structure having the greater structure energy has the lower internal energy and thus is the more stable. From qualitative consideration (Reference 40 and Figure 1), the α structure is more strained, and should therefore have higher structure energy, than the β structure.

If the preceding arguments are valid and α and β silicon nitride are true polymorphs, questions arise as to the transformation temperature and as to why the β/α transformation never has been observed experimentally. The present results indicate that the transition temperature must be less than 1600 C but existing thermodynamic data are inadequate to establish what the exact temperature is. It is possible, however, that the transition temperature could be so low that kinetic barriers could prevent the β/α transformation from ever occurring, especially in view of the considerable disruption necessary to go from one structure to the other. It should also be remembered that the present results as well as those in the literature apply almost exclusively to systems at atmospheric pressure. As has been demonstrated for silicon carbide, for example, there could be another pressure regime in which the transformation could occur reversibly.[43]

43. KIEFFER, A. R., ETTMAYER, P., GUGEL, E., and SCHMIDT, A. *Phase Stability of Silicon Carbide in the Ternary System Si-C-N.* Mater. Res. Bull., v. 4, 1969, p. S153-S156.

In view of the foregoing discussion, the results of Clancy,[44] who presented inferential evidence for the β/α transformation, are difficult to rationalize. In an examination by optical and electron microscopy of silicon nitride crystals obtained from several sources, he found examples of crystals which apparently contained both crystalline phases. Because those crystals had morphologies said to be typical of the β phase, Clancy concluded that they had partially transformed to α silicon nitride. It must be noted, however, that no data were reported on transformation kinetics, i.e., it was not shown that what was observed was indeed β transforming to α over a given period of time. It is therefore possible that the observed crystals were not in fact transforming from β to α, but that they had merely formed from both phases.

SUMMARY

a. A quantitative X-ray technique has been successfully used to evaluate the kinetics of the α/β silicon nitride phase transformation at 1600 C.

b. Significant side reactions to form silicon carbide occur in silicon nitride powder without oxide additions and such reactions proceed particularly quickly in contaminated systems.

c. Additions of magnesia enhance the rate of transformation at 1600 C while additions of yttria do not. Such behavior is consistent with expected liquid phase formation in the former case, and it strongly supports the assumption that the transformation proceeds via a solution-precipitation mechanism.

d. High purity α silicon nitride powder transforms at 1600 C only with magnesia additions.

e. The transformation yields material with a unique microstructure comprising grains that are relatively fine and typically log-shaped.

f. The α/β silicon nitride phase transformation can be classified as a reconstructive transformation of secondary coordination.

g. Existing theories and experimental data indicate that α and β silicon nitride are true polymorphs with the α silicon nitride the low-temperature form.

ACKNOWLEDGMENTS

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